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Synthesis and crystal structure characterization of (E)-2,2,2-Trifluoro-*N*-[2-(2-nitrovinyl)phenyl]acetamide

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ABSTRACT

The title compound, (E)-2,2,2-trifluoro-N-[2-(2-nitrovinyl)phenyl] acetamide, was synthesized and characterized by ^{1}H and ^{13}C NMR and HRMS spectroscopy. Its molecular configuration was investigated by X-ray crystallography. The crystal structure analysis revealed that the structure exhibits intermolecular hydrogen bonds of the type N–H …O and intermolecular hydrogen bonds of the type N–H …F, and molecules are linked by weak C–H …O contacts. Furthermore, the two oxygen atoms of nitro group are disordered over two positions, respectively, with site occupancy factors of 0.8:0.2 and 0.6:0.4. Three fluorine atoms are also disordered over two positions, respectively, one fluorine atom with site occupancy factors of 0.6:0.4 and the other two fluorine atoms with site occupancy factors of 0.5:0.5.

KEYWORDS:
Hydrogen bonding; single crystal; synthesis; X-ray diffraction

Introduction

Nitrostyrenes are versatile intermediates in synthetic organic chemistry as well as in the chemical industry [1, 2]. 2-Amino-nitrostyrenes, as their derivatives bearing both a Michael donor and Michael acceptor, are the new and significant starting materials used in organocatalytic cascade reactions. Such as they are important reactants for the synthesis of a variety of nitroheterocyclic compounds, like dihydroquinolines derivatives [3] and tetrahydroquinoline derivatives [3, 4], which have recognized important pharmaceutical intermediates and have potential for further development as drugs for treating neurological diseases. Additionally, the trifluoromethyl groups own distinctive qualities to biological activities compounds [5, 6]. So, numerous useful methods have been developed for the preparation of nitroolefins [7]. In this paper, the title compound, (E)-2,2,2-trifluoro-N-[2-(2-nitrovinyl)phenyl]acetamide (Fig. 1), was synthesized and characterized by ^{1}H and ^{13}C NMR and HRMS spectroscopy. Its absolute molecular configuration was investigated by X-ray single-crystal diffraction analysis. In the title compound, the dihedral angle between C=C double bond and benzene ring is 16.24(3)°.There is a twist between acetamide group and the benzene ring with the C2-C1-N1-C9 torsion angle being 44.01(4)°.The C7-C8-N2-O3 torsion angle is 16.57(3)°. The C6-C7-C8-N2 torsion angle of 179.75(4)° confirms the E configuration of the molecule with respect to the C7 = C8 double bond. There also exists a small torsion angle 2.84° of the C1-N1-C9-O1.

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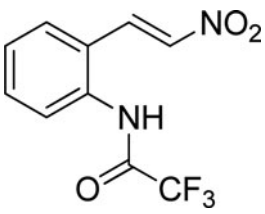


Figure 1. Structure of 2-amino-nitrostyrene.

Table 1. Crystal data and structure refinement parameters of compound (3).

Parameter	Value
CCDC deposition number	1031452
Empirical formula	$C_{10}H_7F_3N_2O_3$
Formula weight	260.18
Temperature	293(2)K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Cell dimensions	$A = 15.609(4)$ Å, $\alpha = 90°$
	$B = 5.0175(12)$ Å, $\beta = 109.902(5)°$
	$C = 14.758(4)$ Å, $\gamma = 90°$
Volume	1086.8(4) Å^3
Z	4
Density (calculated)	1.590
Absorption coefficient	0.151
F_{000}	528
Crystal size	$0.211 \times 0.165 \times 0.123$ mm^3
Theta range for data collection	2.776°–25.498°
Index ranges	$-18 \le h \le 14$
	$-6 \le k \le 6$
	$-17 \le l \le 17$
Reflections collected	5499
Independent reflections	1988 [$R_{int} = 0.0578$]
Absorption correction	$T_{min} = 0.6090$, $T_{max} = 0.7457$
Refinement method	Full-matrix least-squares on $F2$
Data /restraints /parameters	1988/213/61
Goodness of fit on F^2	1.082
Final R indices [$I > 2\sigma$ (I)]	$R_1 = 0.0643$, $\omega R_2 = 0.1590$
R indices (all data)	$R_1 = 0.0807$, $\omega R_2 = 0.1769$
Extinction correction	SHELXL
Flack parameter	None
Largest diff. peak and hole	0.321 and −0.423 e.Å^{-3}

Experimental

^{1}H and ^{13}C NMR were recorded in $CDCl_3$ on Bruker AVANCE III (500 MHz for ^{1}H NMR and 125 MHz for ^{13}C NMR). Proton chemical shifts (δ) are relative to tetramethylsilane (TMS, $\delta = 0.0$) as internal standard and expressed in parts per million. Spin multiplicities are given as *s* (singlet), *d* (doublet), *t* (triplet), and *q* (quartet), as well as *b* (broad). Coupling constants (*J*) are given in hertz. HRMS data were measured on an Agilent 6120 LC/TOF-MS with ESI source.

Synthesis of (E)-2,2,2-Trifluoro-N-[2-(2-nitrovinyl)phenyl]acetamide (3)

A dichloromethane (1.0 mL) solution of 2,2,2-trifluoro-N-(2-formylphenyl)acetamide (1 mmol) and nitromethane (5 mmol) was stirred with piperidine (0.1 mL) as catalyst

Table 2. Atomic coordinates and equivalent thermal parameters of the non-hydrogen atoms (Å^2). U_{eq} = (1/3) $\Sigma\, i\, \Sigma\, j\, Uij a_i * a_j * (a_i . a_j)$.

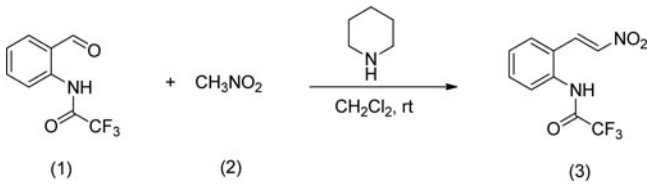
Atom	*x*	*Y*	*z*	U_{eq}
N1	0.33100(13)	0.7681(4)	0.18961(13)	0.0462(5)
N2	0.08866(14)	0.0969(4)	0.16006(15)	0.0560(6)
O1	0.35430(16)	1.2064(3)	0.22522(15)	0.0815(7)
O2	0.0373(6)	-0.0880(16)	0.1282(7)	0.0654(17)
O3	0.1090(5)	0.1719(13)	0.2457(5)	0.0820(16)
O2′	0.037(3)	-0.094(8)	0.145(4)	0.075(4)
O3′	0.1470(6)	0.099(2)	0.2402(7)	0.086(2)
F1	0.4075(9)	1.049(2)	0.4139(11)	0.086(3)
F2	0.4285(8)	0.650(3)	0.3727(10)	0.081(2)
F3	0.5118(9)	0.974(2)	0.3628(11)	0.089(2)
F1′	0.3887(6)	0.9755(17)	0.4103(7)	0.091(2)
F2′	0.4530(7)	0.657(3)	0.3603(9)	0.088(3)
F3′	0.5041(9)	1.0536(19)	0.3709(11)	0.081(2)
C1	0.27445(14)	0.7920(4)	0.09104(15)	0.0432(5)
C2	0.29818(17)	0.9683(5)	0.03141(18)	0.0532(6)
C3	0.24354(19)	0.9927(5)	-0.06391(19)	0.0611(7)
C4	0.16752(18)	0.8353(5)	-0.10059(17)	0.0605(7)
C5	0.14539(16)	0.6553(5)	-0.04258(16)	0.0523(6)
C6	0.19719(14)	0.6315(4)	0.05510(15)	0.0429(5)
C7	0.16930(15)	0.4535(4)	0.11802(16)	0.0472(6)
C8	0.11016(14)	0.2593(4)	0.09098(16)	0.0469(6)
C9	0.36670(15)	0.9735(4)	0.24662(17)	0.0494(6)
C10	0.42833(17)	0.9072(5)	0.34849(19)	0.0548(6)

Table 3. Bond lengths (Å).

Atoms	Length	Atoms	Length
N1–C9	1.327(3)	C1–C2	1.384(3)
N1–C1	1.427(3)	C1–C6	1.396(3)
N1–H1	0.77(3)	C2–C3	1.380(4)
N2–O2′	1.23(2)	C2–H2	0.9300
N2–O3′	1.223(10)	C3–C4	1.374(4)
N2–O2	1.212(6)	C3–H3	0.9300
N2–O3	1.252(6)	C4–C5	1.367(3)
N2–C8	1.431(3)	C4–H4	0.9300
O1–C9	1.209(3)	C5–C6	1.397(3)
F1–C10	1.326(15)	C5–H5	0.9300
F2–C10	1.337(15)	C6–C7	1.458(3)
F3–C10	1.290(14)	C7–C8	1.308(3)
F1′–C10	1.310(11)	C7–H7	0.9300
F2′–C10	1.308(15)	C8–H8	0.9300
F3′–C10	1.335(13)	C9–C10	1.520(3)

at room temperature. After completion of the reaction, the mixture was extracted with dichloromethane and washed by aq HCl(1M).The solvents were removed under vacuum and the residue was purified by column chromatography on silicagel [eluent: petroleum ether-ethyl acetate(3:1)] (Scheme 1).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.054–8.027 (m, 2H), 7.681–7.539 (m, 4H), 7.462–7.432 (m, 1H) ppm; **^{13}C NMR** (125 MHz, DMSO): δ = 155.74 (*d*, *J* = 36.9 Hz), 139.122, 134.914, 133.812, 132.468, 128.370, 127.972, 127.634, 126.024, 115.840 (*d*, *J* = 286.9 Hz) ppm; **HRMS:** (ESI+) *m*/*z* calcd for $[C_{10}H_8F_3N_2O_3]^+$ 261.0487, found 261.0490. Scheme 1



Scheme 1. Synthesis of 2-amino-nitrostyrene.

Table 4. Bond angles (°).

Atoms	Angle	Atoms	Angle
C9-N1-C1	124.1(2)	C1–C6-C5	117.7(2)
C9–N1-H1	117.1(18)	C1-C6-C7	121.21(19)
C1-N1-H1	118.6(18)	C5-C6-C7	121.07(19)
O2′-N2-O3′	114(3)	C8-C7-C6	126.5(2)
O2-N2-O3	121.9(6)	C8-C7-H7	116.7
O2′-N2-C8	128(2)	C6-C7-H7	116.7
O3′-N2-C8	114.0(5)	C7-C8-N2	121.3(2)
O2-N2-C8	116.4(5)	C7-C8-H8	119.4
O3-N2-C8	120.5(4)	N2-C8-H8	119.4
C2-C1-C6	120.7(2)	O1-C9-N1	126.1(2)
C2-C1-N1	119.7(2)	O1-C9-C10	117.5(2)
C6-C1-N1	119.56(19)	N1-C9-C10	116.4(2)
C3-C2-C1	119.9(2)	F2′-C10-F1′	110.2(7)
C3-C2-H2	120.0	F3-C10-F1	103.0(8)
C1-C2-H2	120.0	F2′-C10-F3′	107.4(7)
C4-C3-C2	120.1(2)	F1′-C10-F3′	105.8(7)
C4-C3-H3	119.9	F3-C10-F2	107.2(8)
C2-C3-H3	119.9	F1-C10-F2	107.7(8)
C5-C4-C3	120.1(2)	F3-C10-C9	111.7(7)
C5-C4-H4	119.9	F2′-C10-C9	113.6(6)
C3-C4-H4	119.9	F1′-C10-C9	110.0(5)
C4-C5-C6	121.4(2)	F1-C10-C9	111.9(6)
C4-C5-H5	119.3	F3′-C10-C9	109.5(7)
C6-C5-H5	119.3	F2-C10-C9	114.7(6)

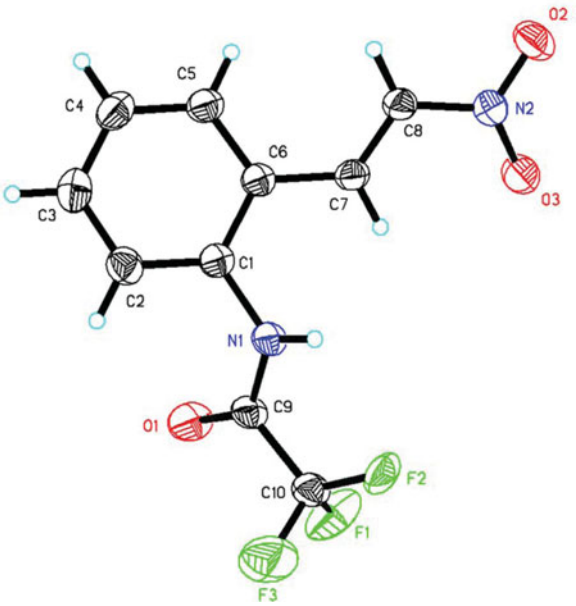


Figure 2. ORTEP of the molecule with thermal ellipsoids drawn at 50% probability.

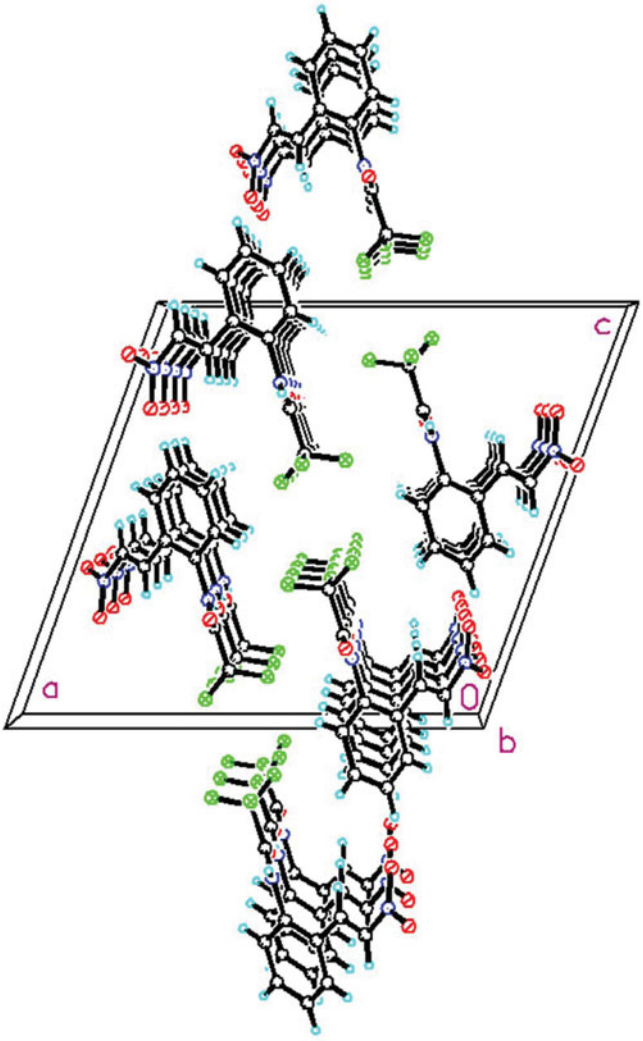


Figure 3. The crystal packing of the title compound (3).

Crystal structure analysis

The crystal structure of the title compound was solved by direct methods and was refined by a full-matrix least-squares method on F^2. A summary of the salient crystallographic data is given in Table 1.

A single crystal suitable for X-ray diffraction (XRD) obtained in ethyl acetate and hexane (V/V = 2:1) was colorless and black. The single crystal XRD of the crystal was collected on Bruker SMART [8] diffractometer at 293(2) K using graphite-monochromated Mo *Kα* radiation (λ = 0.71073 Å). The cell was refined on Bruker SMART [8] and the data were reducted on Bruker SHELXTL [9] and the structure was refined on SHELXL-2013 [10]. The structure was solved by direct methods using full-matrix least-squares on *F*2. Subsequent refinements were carried out with anisotropic thermal parameters for nonhydrogen atoms. H atoms were placed in calculated position with all C–H = 0.93 Å, N–H = 0.77Å. All H atoms were included in the final cycles of refinement as riding mode, with Uiso(H) = 1.2 Ueq of the carrier atoms. The software used to prepare material for publication was Bruker SHELXTL [9].

Table 2 gives the atomic coordinates and equivalent thermal parameters of the nonhydrogen atoms. Tables 3 and 4 give the list of bond lengths and bond angles, respectively.

The ORTEP of the molecule with thermal ellipsoids drawn at 50% probability is shown in Fig. 2. The crystal structure analysis revealed that the structure exhibits intramolecular hydrogen bonds of the type N1–H1 …F. The nitroalkene has an *E* conformation, and the dihedral angle between C=C double bond and benzene ring is 16.24(3)°.There is a twist between acetamide group and the benzene ring with the C2–C1-N1-C9 torsion angle being 44.01(4)°.The C7–C8-N2-O3 torsion angle is 16.57(3)°. The C6-C7-C8-N2 torsion angle of 179.75(4)° confirms the *E* configuration of the molecule with respect to the C7 = C8 double bond. There also exists a small torsion angle 2.84° of the C1-N1-C9-O1. The packing diagram of (3) is given in Fig. 3.

Conclusion

The title compound, (E)-2,2,2-trifluoro-N-[2-(2-nitrovinyl)phenyl]acetamide (3), was synthesized and characterized by ^{1}H and ^{13}C NMR and HRMS spectroscopy. We summarized the results from XRD measurements for compound (3) single crystal. X-ray analysis revealed that the nitroalkene has an *E* conformation and the molecules are linked by weak intermolecular and intramolecular H bonding interactions. Furthermore, in the title compound, two oxygen atoms of nitro group and three fluorine atoms are disordered over two positions.

Supplementary Information

CCDC 1031452 contains the supplementary crystallographic data for this article. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html, or from The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

Fax:+44(0)1223-336033. E-mail: deposit@ccdc.cam.ac.uk.

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